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Liquid crystal properties resulting from synergetic effects between non-mesogenic organic molecules and a one nanometre sized octahedral transition metal cluster†

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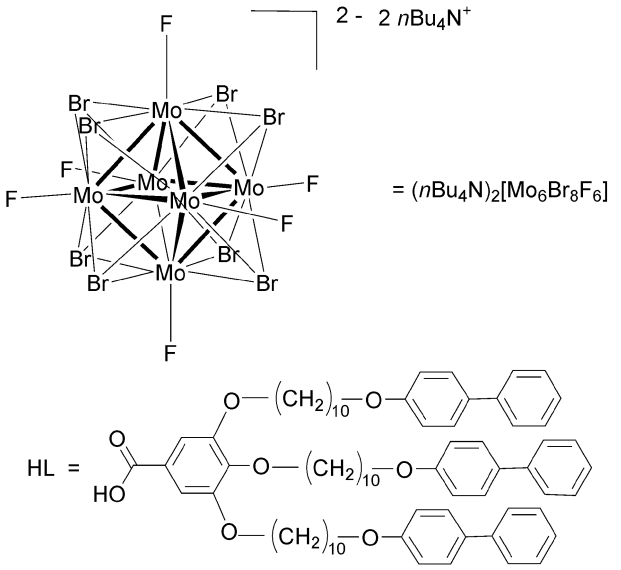
This work presents the synthesis and studies of a red-NIR luminescent liquid crystal compound based on an octahedral metallic cluster core orthogonally bounded to six non-mesogenic organic ligands. It evidences synergetic effects between the organic and inorganic parts of the hybrid, resulting in the generation of liquid crystal properties on cooling from the isotropic melt.

Luminescent liquid crystals have a great potential to be used in electro-optical devices and, besides the purely organic liquid crystalline systems investigated so far,[1] recent results showed that metallomesogens[2] (liquid crystalline materials incorporating metal ions) are very good candidates for such multifunctional materials.[3] In this perspective, the incorporation of octahedral transition metal clusters into liquid crystals (LC) is expected to lead to very interesting emissive properties taking into account that these clusters (Mo_6, Re_6 and W_6) are highly emissive in the red-NIR area displaying long excited state lifetimes with photoluminescence quantum yields up to 0.23.[4,5] Moreover, the emissive excited state of cluster-based compounds is mainly metal centered[5] and therefore neither the coordination of promesogenic ligands onto the metallic octahedron nor intermolecular interactions should affect significantly their emission properties. Let us recall that octahedral M_6 cluster building blocks, obtained *via* high temperature solid state synthesis,[6] can be introduced either directly[7] or after functionalisation[8,9] in supramolecular assemblies or materials, without significant alterations of their intrinsic properties (luminescence, redox). We recently reported the first example of a clustomesogen consisting of a Mo_6X_8 cluster core modified with six gallate derivatives containing three long alkyl chains terminated by cyanobiphenyl (CNBP) units.[10] This compound was obtained together with 6 HF molecules by heating a mixture containing the corresponding gallic acid and a hexafluorinated cluster. We showed that a smectic phase could be induced by grafting mesomorphic units onto the cluster through a flexible aliphatic spacer. Our aim in this work is to understand whether the cluster core, despite its bulkiness and its octahedral coordination sphere, can induce the formation of liquid crystal phases when non-mesomorphic ligands are grafted onto it. Such behaviour has already been reported for metallomesogens containing mononuclear complexes.[11] We present herein, the synthesis, characterisation and mesogenic properties of a Mo_6 cluster substituted by six non-mesomorphic ligands based on a gallic acid scaffold modified with three oxydecamethyleneoxybiphenyl arms (HL, Scheme 1). The biphenyl unit (BP) is widely used in the construction of main-chain or side-chain polymers with liquid crystal properties, or able to control the liquid crystals surface alignment. It is used mainly as a core unit and, in few



Scheme 1 Representation of the $(nBu_4N)_2[Mo_6Br_8F_6]$ cluster precursor and the HL organic ligand used in this work.

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cases, as a mesogenic terminal group linked through a spacer to the polymer backbone.[12] In our case however, Differential Scanning Calorimetry (DSC) and Polarised Optical Microscopy (POM) experiments showed that HL does not have liquid crystal properties.

HL was obtained in three steps following reported procedures for similar compounds.[10] The grafting procedure of HL on the cluster core was slightly modified compared to that reported earlier[10] in order to eliminate the HF by-product (see ESI†). Indeed, the use of triethylamine during the reaction, combined to a washing of the organic phase with an aqueous solution, allows the removal of HF. ^{19}F NMR experiments revealed the loss of all fluorine atoms, ^{1}H NMR showed a small downfield shift of the singlet signal corresponding to the aromatic proton of the gallic moiety of HL from 7.34 ppm to 7.37 ppm; IR spectroscopy confirmed the monodentate ligation of the carboxylate through the creation of a M–O single bond with the shift of the $\nu_{C=O}$ stretching band from 1687 cm^{-1} for the free acid to 1630 cm^{-1} for the hybrid.[9,10,13] The stoichiometry was further confirmed by elemental analysis (see ESI†).

The liquid crystal properties of $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6Br_8L_6}]$ were investigated by POM, DSC and X-ray diffraction. The thermal data are summarized in Table 1. The assignment of the observed liquid crystalline phase to a layered SmA phase was done in a first attempt by temperature dependent POM observations where a typical fan-shaped texture with several homeotropic regions developed on cooling from the isotropic liquid (inset Fig. 1). The modified cluster melts straight to the isotropic liquid. On cooling at 10 °C min^{-1}, three exothermic peaks were present in the DSC thermogram (see ESI†). The first one, a relatively sharp peak at 80 °C, corresponds to the transition from the isotropic liquid to a liquid crystal phase, while the two others correspond to successive transitions to crystalline phases at 67 °C and 51 °C. The enthalpy change of the I–SmA transition is 57.9 kJ mol^{-1} which is a very high value when compared to the normal range of such transition.[14] However, this class of compounds may be regarded in the light of first generation dendrimers containing a Mo_6 cluster rigid core. Therefore, if the enthalpy change is divided by the number of mesogenic groups (18), it yields to a value of 3.3 kJ mol^{-1} per mesogenic unit which perfectly matches the range of I–SmA transitions.[15] Such approach was successfully employed in the case of fullerene[15,16] or silsesquioxane[17] containing liquid crystal dendrimers.[18] The second heating cycle shows one exothermic peak between two endothermic peaks which is indicative of a double melting behaviour (see ESI†).[19]

Table 1 Thermal data for HL and $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6Br_8L_6}]$ obtained by DSC at 10 °C min^{-1}

Compound	Transition	T^c/°C	ΔH/kJ mol^{-1}
HL	Cr–Cr′	101	119.2
	Cr′–I	118	55.1
	I–Cr	85	76.6
	Cr–I	109[a,b]	78.8
$(n\mathrm{Bu_4N})_2[\mathrm{Mo_6Br_8L_6}]$	Cr–I	82	280.6
	(I–SmA)	(80)	(57.9)
	(SmA–Cr)	(67)	(22.6)
	(Cr–Cr′)	(51)	(34.4)

[a] Data taken from the second heating cycle. [b] On the second heating cycle there still can be seen a small peak with T_{max} = 120 °C that corresponds to the melting of the Cr′ form (see Fig. S7 in the ESI†), information that is supported by POM observations. [c] These values represent T_{onset} taken from DSC measurements.

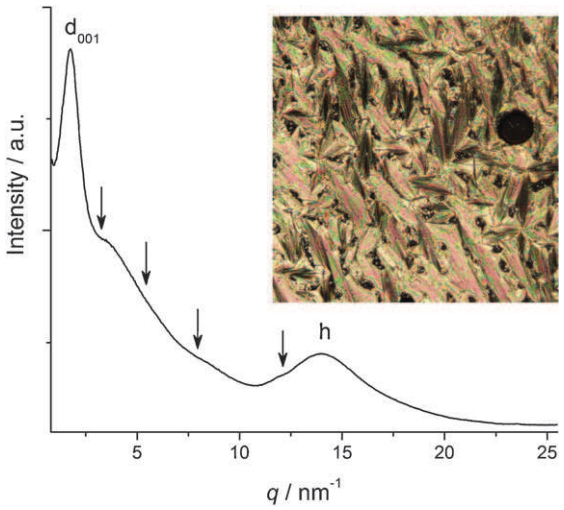

Fig. 1 X-Ray diffraction pattern of $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6Br_8L_6}]$ at 70 °C obtained on cooling from the isotropic (the arrows indicate the position of the reflections relative to the clusters organisation within the layers) liquid. Inset: polarized optical micrograph of $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6Br_8L_6}]$ at 82 °C.

To gain more insights regarding the arrangement of the molecules in the mesophase, temperature-dependent X-ray diffraction measurements were carried out (Fig. 1). At 70 °C, the X-ray diffraction pattern of the mesophase contains a single and broad peak in the low angle region, assigned to the (001) diffraction plane and corresponding to a lamellar structure with an inter-layer distance of 35.7 Å. The fact that this signal is much broader than its equivalent in the X-ray pattern of its CNBP–Mo_6 analogue is probably due to the ability of CNBP mesogenic groups for better defining the lamellar nature of the mesophase. Indeed, it is frequently observed that CNBP units will lead to layered phases when grafted as side chains onto a polymer or as terminally appended units in dendrimers.[18] The diffuse scattering halo in the wide angle region centered around 4.5 Å (*h* in Fig. 1) corresponds to the lateral short range order of the molten chains and the biphenyl moieties, confirming the liquid crystalline nature of the mesophase. Besides these two signals, additional very broad and intense reflections are observed. Although the appearance of such reflections may indicate some kind of local ordering of the clusters within the layers, the reflections broadness excludes any clear geometrical interpretation. However, by analogy with previously reported results,[10] one might expect an orientation of the modified clusters with their C_3 axis perpendicular to the plane of the layers and an equal repartition of the organic ligands on both sides of the metallic core. So far, if we compare the results obtained for $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6Br_8L_6}]$ and for its CNBP–Mo_6 analogue,[10] we can notice that the lack of cyano groups has a dramatic impact on the mesomorphic behaviour of the obtained hybrid: (i) the destabilisation of the mesophase, (ii) a significant narrowing of the mesomorphic temperature range from approximately 83 °C for the CNBP analogue to 17 °C for $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6Br_8L_6}]$ and, (iii) a one nanometre shortening of

the lamellar interlayer distance which, according to molecular modelling (by means of Hyperchem software), may correspond to a higher interdigitation of the BP moieties. This last point is corroborated with the X-ray diffraction patterns obtained below 70 °C.

Indeed, lowering the temperature to 60 °C (first crystalline phase) is traduced on the X-ray diffraction pattern by an increase of the interlayer distance and by the appearance of a signal located at 3.18 Å relative to π–π stacking interactions of the biphenyl moieties (see ESI†). Let us note that, such impact on mesogenic properties by removal of CN groups has been previously reported for amphiphilic liquid crystalline oligomers based on semiperfluorinated ester derivatives of gallic acid.[20]

As the emissive excited state of Mo_6 clusters is mainly metal centered,[21] the coordination of organic ligands onto the six metal atoms should not induce significant changes in the emission properties of the cluster core. Therefore, emission measurements were carried out for $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6Br_8L_6}]$ on a sample deposited by spin coating on a silicon wafer, heated at 90 °C and cooled to room temperature. $(n\mathrm{Bu_4N})_2[\mathrm{Mo_6Br_8L_6}]$ shows the same broad emission, from 550 to nearly 900 nm with a maximum located at 740 nm than its fluoride precursor, for a wide range of excitation wavelength starting from 300 nm to 550 nm (see ESI†). This similar behaviour upon light excitation is of significant importance because it shows that different types of ligands can be used to modify the liquid crystalline properties of the clustomesogens without altering their luminescence properties. Yet, it gives them a major advantage on metallomesogens containing d-block elements for which, most of the emissive excited states are not metal centred and thus, for which the emission is strongly affected by the nature of the ligands and the intramolecular interactions occurring in the mesophase.[22]

In conclusion, we have shown in this work that, despite its octahedral coordination sphere and its bulkiness, a one nanometre sized octahedral transition metal cluster can promote the formation of a liquid crystal phase when it is bounded to six non-liquid crystal organic ligands. The intrinsic luminescence properties of the cluster core are not significantly modified by the grafting of the organic ligands and are not influenced by intermolecular interactions existing either in the mesomorphic or crystalline phase. These two important results open new and fascinating perspectives in the design of other type of clustomesogen for which these evidenced synergetic effects between the metallic core and the organic bounded ligands will play an essential role in the behaviour of the resulting organic–inorganic hybrid nanomaterial.

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